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# AN EXPERIMENTAL STUDY ON CLAY FORMATION AND WEATHERING OF FELSPARS.

## Preface.

I n 1927, at the laboratory of the Swedish Institute of Experimental Forestry, I began an experimental investigation into the chemical weathering of silicate minerals. In the same year I obtained a grant from the Royal Swedish Academy of Science for the purpose of procuring some apparatus for the investigation. Afterwards, in 1928, the International Education Board awarded me a fellowship, which enabled me to spend about five months under Professor Dr N. BJERRUM at the chemical laboratory of the Royal Veterinary and Agricultural College in Copenhagen. He instructed me in certain physico-chemical methods, which were then being applied to the above-mentioned problem. During the whole of this time I had the great advantage of working under his guidance. I have also derived much help from the methods employed by Mr. H. RIEHM in an investigation into the nature of clay carried out at Professor BJERRUM's laboratory, the results of which have not as yet been published. Mr. A. LANNUNG and Mr. C. JÖRGENSEN, in Copenhagen, and Mr. A. BILLBERG, in Stockholm have rendered me valuable assistance in procuring and setting up various apparatuses.

Although my work does not strictly fall within the programme of the Swedish Institute of Experimental Forestry, and was carried out at the chemical laboratory of the Royal Veterinary and Agricultural College in Copenhagen, the Director of the Institute, Professor Dr H. HESSELMAN, has allowed me to publish it in their reports.

To all the above-named persons and institutions and more especially to Professor BJERRUM, I wish to offer my warm and sincere thanks.

The chemical laboratory of the Royal Veterinary and Agricultural College in Copenhagen, July 1928.

OLOF TAMM.

## Introduction.

In 1879, Mr. DAUBRÉE, the geologist, published his experiments on the grinding of orthoclase in water. He rotated 5 kilograms of orthoclase and water in an iron cylinder for 192 hours, when much of the mineral had disintegrated into a fine silt, and 12.6 g. of potash had been dissolved by the water. More recently I (1925, 1928) have shown that granite materials, quartz, felspar and biotite, when treated in the same way, are disintegrated into very small particles that possess a high hygroscopicity. From granite and biotite the product was a clay, which in many respects closely resembled natural clay. The method seems to be of general application for disintegrating hard matter into very small particles and should be suitable for studying the chemical properties of silicate minerals. The present paper describes a first attempt in this direction.

## The Minerals investigated.

Two feldspars, microcline and oligoclase, both from the Ytterby mine in the neighbourhood of Stockholm were employed. These feldspars have been described and analysed by I. NORDENSKJÖLD (1910):

Microcline from Ytterby.

	1.	2.	3.
SiO <sub>2</sub> .....	64.32 %	64.40	64.57
Al <sub>2</sub> O <sub>3</sub> .....	19.41	19.30	19.73
Fe <sub>2</sub> O <sub>3</sub> .....	0.14	0.30	0.20
CaO.....	—	0.40	0.18
MgO.....	0.35	—	—
K <sub>2</sub> O.....	12.90	12.56	12.26
Na <sub>2</sub> O.....	2.10	2.68	3.06
Loss. on Ignition.....	0.57	—	—
Total	99.79	99.64	100.00

Oligoclase from Ytterby.

	1.	2.	3.	4.	5.	6.	7.	8.
SiO <sub>2</sub> .....	61.55	64.23	63.19	62.81	63.66	64.81	63.38	63.00
Al <sub>2</sub> O <sub>3</sub> .....	23.80	23.57	23.52	23.21	23.45	22.99	22.98	23.00
Fe <sub>2</sub> O <sub>3</sub> .....	—	—	—	0.10	—	—	—	0.30
CaO.....	3.18	2.81	4.81	3.81	3.53	3.15	3.63	2.60
MgO.....	0.80	—	—	0.18	0.05	—	—	0.03
K <sub>2</sub> O.....	0.38	0.81	—	0.58	1.59	0.82	0.55	0.38
Na <sub>2</sub> O.....	9.67	8.47	9.01	8.18	7.91	8.89	9.10	10.84
Loss. on Ignition...	—	—	—	0.81	—	—	0.37	—
Total	99.38	99.89	100.53	99.68	100.19	100.66	100.01	100.15

### The Method of Disintegration.

The felspar was crushed into fragments, which at the start were sharply edged. Only the fragments of 5—15 millimetres size were employed. The disintegration was carried out in cylinders, which had an internal diameter of 35—45 millimetres and a length of 160—170 millimetres. In some of the experiments a cylinder of pure silver (0.10 per cent impurities) was employed, in others cylinders of transparent quartz glass, in others a cylinder of oligoclase from Ytterby. It was impossible to make a cylinder of the microcline. The quartz glass cylinders were closed by brass lids, covered with a layer of paraffin, two millimetres thick. Just as the paraffin had solidified, but was still soft, the lid was pressed against the end of the cylinder, which was then painted on the outside with liquid paraffin. The cylinder could thus be hermetically sealed. The paraffin layer was not attacked mechanically during the disintegration. The silver cylinder was closed by a silver lid in the same way. The oligoclase cylinder, which was made from a large oligoclase crystal by diamond boring, was closed by the cylindrical piece of the mineral, which was formed during the boring, surrounded by a caoutchouc tube, (fig. 1). This cylinder was only employed in experiments with oligoclase, and in these, pieces of the same crystal from which the cylinder was made, were disintegrated.

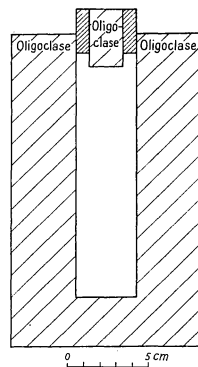


Fig. 1. Cross section of oligoclase cylinder.

The water employed was carefully distilled as for electric conductivity measurements. The required quantity of water was poured into the rotation cylinder, and any traces of carbon dioxide were removed by passing a rapid stream of  $\text{CO}_2$ -free air through the water for at least an hour. The felspar pieces were introduced into the liquid while the air stream continued, after which the cylinder was closed very rapidly. In this way it was possible to avoid the influence of carbon dioxide on the disintegration process in the cylinder. In the experiments with the oligoclase cylinder it is, however, conceivable that the caoutchouc may have given off traces of carbon dioxide to the liquid.

The cylinders, charged with felspar and water, were rotated with a speed of 90 rotations per minute. Considerable heat was generated in the cylinders during the rotation, causing a rise of temperature. To avoid this, the cylinders of silver and quartz glass were placed in a vessel of water kept at a constant temperature of  $20^\circ\text{C}$ ., and the rotations

were made in this vessel. The rotations of the oligoclase cylinder were carried out in air at room temperature ( $17^{\circ}$ — $18^{\circ}$  C.).

The quartz glass, as well as the silver and oligoclase, was strongly attacked mechanically during the rotation. The quartz cylinder soon became opaque. A small amount of the silver was dispersed into colloid particles, which formed a black suspension. A sample of such a suspension had not settled 4 months later. The felspar particles, which were formed in the quartz or silver cylinders were thus contaminated respectively with quartz or silver. By accurately weighing the cylinders before and after the experiments, the extent of their decomposition was determined.

In the experiments in which the oligoclase cylinder was used, the caoutchouc tube, like the paraffin, was not attacked mechanically during the disintegration. A stopper of caoutchouc only could be used without its being attacked if it was of a high quality. Caoutchouc of inferior quality underwent a slight decomposition, which could be detected by its odour in the suspension obtained — a certain and sensitive test for small quantities of this substance.

The effectiveness of the disintegration of the felspar depends largely on the shape of the fragments. After a few hours rotation the edges were rubbed off and the pieces got rounder the longer the rotation was continued. When the pieces are edged, they give much more silt and clay than after they have been rounded, but the round pieces give smaller particles than the edged ones (see p. 17). If several successive rotation experiments are carried out with the same felspar pieces, the quantity of particles formed per hour sinks. An experiment in the silver cylinder gave 0.0354 grams of particles per hour, another with the same pieces rounded, 0.0081 grams per hour.

### The Mechanical Result of the Disintegration.

**Microcline.** (Rotation experiment, microcline No. 13). 100 g. felspar fragments were rotated in 50 c. c. pure water in a quartz glass cylinder for 108 hours at  $20^{\circ}$  C. 3.27 g. felspar and 0.57 g. quartz glass from the cylinder were disintegrated into particles. The product was separated from the liquid by ultrafiltration through a coarse membrane filter from *Membranfiltergesellschaft in Göttingen*, and suspended in water, and the whole was shaken for several hours until the particles were completely dispersed in the water. The suspension obtained contained 14.9 % quartz and 85.1 % felspar. The small quantities of chemical products, formed during the disintegration, are not taken into account here (table 2,

p. 8). Half the suspension was allowed to settle in a glass cylinder, with the falling height of 10 cm, for 8 hours. Thereafter the liquid was poured off by means of a siphon, the settled particles were suspended in a fresh amount of distilled water, left to settle 10 cm in 8 hours, the liquid poured off, and so on. In this way all the particles of a size greater than  $2\ \mu$  were removed, according to the method of ATTERBERG (1912). The method, however, should be considered as very rough. Only 0.08 g. corresponding to 4.6 % of the disintegration product was found to have a size  $> 2\ \mu$ . In what follows, this fraction is called *D*.

The particles, which had a size less than  $2\ \mu$ , were divided by the aid of a centrifuge (about 2500 rotations per minute for 3 minutes, radius 14—22 cm) into two fractions, *A* and *B*, of which *A* was the most finely ground. *A* amounted to 0.495 g. or 28.2 % of the whole disintegration product. Its water content was determined as follows: *A* measured volume of the suspension, containing *A*, was evaporated on the water-bath in a platinum vessel and then dried at  $105^{\circ}$ — $110^{\circ}$  C. and weighed. Then it was heated to dark red-glowing and weighed again. The water content was found to be 3.7 %. The water content of the feldspar itself was only 0.02 %, determined on the pulverized mineral by the same method. The water content of the different disintegration products, which are given further on, have been determined by heating to dark red-glowing after drying in two different ways: at  $105^{\circ}$ — $110^{\circ}$  C. in the air, and at room temperature in vacuo over  $\text{H}_2\text{SO}_4$ . These two drying methods have always given concordant results.

The average size of the particles was determined in the ultra-microscope by counting the number of particles in a known volume of the suspension. The specific gravity of microcline is 2.60 and that of the particles was assumed to be the same. Their form was assumed to be spherical. The number of particles in the sample to be investigated was chosen so that on the average 3—4 particles were found simultaneously in the known volume under the microscope. The number of particles was determined every 4 seconds at least 50 times. The particles exhibited rapid Brownian movement. Some of them showed a slight tendency to settle. Hence the smallest value found for their average diameter may be the most probable one. Four determinations gave the values for the average diameter of the particles:  $0.48\ \mu$ ,  $0.47\ \mu$ ,  $0.56\ \mu$ ,  $0.58\ \mu$ .

The fraction *B* amounted to 1.18 g. or 67.2 % of the whole grinding product. The average diameter of its particles was found to be  $0.82\ \mu$  in the ultra-microscope. The particles of the whole disintegration product before separation were found to have an average diameter of  $0.62\ \mu$ .



**Oligoclase.** (Rotation experiment, oligoclase No. 1). 75 g. felspar and 25 c. c. water were rotated for 140 hours in the oligoclase cylinder (at room temperature, about 90 rotations per minute). 8.09 grams of the oligoclase fragments and 3.19 grams of the cylinder were disintegrated, total 11.28 grams. This is thus the weight of the oligoclase particles formed, if no account is taken of the products of chemical reactions during the disintegration (table 3, p. 8). The particles were separated from the liquid by ultrafiltration and dispersed in water. The suspension obtained had a volume of 250 c. c. 10 c. c. of it was found to contain 0.45 g. particles, after heating to dark red-glowing. This corresponds with 11.3 g. particles in the whole liquid, thus the same value as given above, which was calculated by weighing the felspar and the cylinder before and after the rotation. 100 c. c. of the suspension was fractionated by ATTERBERG'S method. It was found that 6.0 % or 0.27 g. had a size  $> 2 \mu$ . This fraction is further on called *G*.

The main part of the disintegration product had a size smaller than  $2 \mu$ . It was separated with the centrifuge into three fractions: *A*, *E*, and *F*, of which *A* was the finest and *F* the coarsest. The average size of the particles was determined in the ultra-microscope, and the water contents were determined by the methods described above. The particles were assumed to be spherical, and their specific gravity 2.64 (i. e. that of oligoclase). The water content of pulverized oligoclase was 0.15 %. The results are given in table 1.

Table 1. The size and the water content of the oligoclase particles.

Fraction	Percent of total disintegration product	Average diameter of particles	Water content of particles
<i>G</i> .....	6.0	$> 2.0 \mu$	not determined
<i>F</i> .....	36.5	$1.06 \mu$	1.3 %
<i>E</i> .....	27.0	$0.57 \mu$	1.6 %
<i>A</i> .....	30.5	$0.44 \mu$	2.5 %

It was immediately obvious under the ultra-microscope that, both with microcline and oligoclase, particles of many different sizes were present in each fraction, especially in the finest. It is therefore probable that the lower limit of the size of the particles lies rather much under the observed average value, especially in the finest fractions. On the other hand it is unlikely that the upper limit in the whole disintegration product lies much over  $2 \mu$  for only a few percentages of all the particles have a size over that value. It may thus be assumed that the size of the particles in general lies between  $0.2 \mu$  and  $2 \mu$ , i. e. within dimensions that are characteristic of natural clays.

By rotation of fragments of feldspars in water these minerals could be disintegrated into particles of dimensions between  $2\ \mu$  and  $0.2\ \mu$ . These dimensions are characteristic of natural clays. The yield of particles over  $2\ \mu$  or below  $0.2\ \mu$  was negligible.

### Chemical Processes during the Disintegration.

As in the experiments of DAUBRÉE, a chemical decomposition takes place during the disintegration, and the water thereby acquires an alkaline reaction. This process was studied by investigating the potential difference  $\varepsilon$  between a platinum-hydrogen electrode in the suspension obtained and a 0.1 N mercurous chloride electrode. The junction between the electrodes was a 3.5 N solution of KCl. For calculating the  $p_H$ -values the formula:

$$p_H = \frac{\varepsilon - 0.3367}{0.0001984\ T}$$

was employed.  $T$  is the absolute temperature. A bridge was used for the determinations, which were accurate within  $0.02\ p_H$ . The calculations were made by the aid of a slide rule.

Great care was taken to avoid the entrance of carbon dioxide from the atmosphere into the liquid before and during the determination. This could be attained, if the cylinder was very quickly opened and 25 or 10 c. c. of the liquid rapidly pipetted off into the electrode vessel, in which the passage of a strong current of hydrogen prevented the access of air to the liquid. After the  $p_H$  had been determined, another part of the suspension was filtered through a coarse membrane filter (from *Membranfiltergesellschaft in Göttingen*). Sometimes a little of the finest particles went through the pores of the filter. After some minutes, however, the filtrate became clear. The turbid filtrate was then poured back on to the filter and a perfectly clear liquid was obtained. 25 c. c. of this was titrated electrometrically with 0.1 N HCl until the reaction was strongly acid,  $p_H = 3$  or 4. At this  $p_H$ , the  $CO_2$ , which had been absorbed by the liquid during the filtration, was completely removed by passing a stream of hydrogen for 45 minutes. Thereafter the liquid was titrated electrometrically with 0.1 N KOH to  $p_H$  12 (fig. 2). This last titration gave the true titration curve for the  $CO_2$ -free solution. The  $p_H$  was determined during the titrations at intervals of 3 minutes and the HCl or KOH was poured into the liquid immediately after the determination had been made.

Table 2. Rotation Experiments with Microcline in 50 c. c. Pure Water.

∞

No. of expt, micro- cline	Cylinder of	Felspar g.	Hours of rotation	Disintegrated fel- spar, in		Amount of cylin- der dis- integrated g.	pH of suspension	Bases dissolved in disintegration (calcd as K), in		Dissolved bases (Calcd as K), in % of disinte- grated fel- spar	Dissolved base-equa- lents, in % of disintegrated felspar's base equivalents
				g.	g. per hour			g. K	milliequiva- lents		
15	Ag	100.13	44	0.39	0.009	0.23	10.09	0.0009	0.022	0.22	1.60
16	»	99.74	89	0.77	0.009	0.39	10.39	0.0017	0.044	0.22	1.60
10	»	150.05	52	0.93	0.018	0.21	10.36	0.0016	0.040	0.17	1.22
24	»	99.97	20	1.48	0.074	0.39	10.41	0.0038	0.098	0.26	1.87
18	»	100.64	280	2.26	0.008	1.21	10.51	0.0039	0.100	0.17	1.25
13	SiO <sub>2</sub>	100.26	108	3.27	0.030	0.57	10.45	0.0054	0.138	0.17	1.19
28	»	100.10	195	3.80	0.020	not determ.	10.43	0.0043	0.110	0.11	0.82
12	Ag	101.11	258	9.13	0.035	1.55	10.63	0.0047	0.120	0.05	0.37
27	»	100.00	530	10.88	0.020	4.27	10.68	0.0117	0.296	0.11	0.78
30	SiO <sub>2</sub>	100.07	90	3.17	0.035	0.28	10.48	not determ.	not determ.	—	—
32	»	96.99	66	3.43	0.052	not determ.	10.55	»	»	—	—

OIOF TAMM

Table 3. Rotation Experiments with oligoclase in Pure Water.

No. of expt, oligoclase	Cylinder of	Felspar g.	Water c. c.	Hours of rotation	Disintegrated fel- spar, in		pH of suspension	Bases dissolved in disintegration (calcd as Na), in		Dissolved bases (as Na), in % of disinte- grated fel- spar	Dissolved base-equa- lents, in % of disintegrated felspar's base equivalents
					g.	g. per hour		g. Na	milliequiva- lents		
10	oligoclase	75.04	50	70	0.87	0.012	10.47	not determ.	—	—	—
11	Ag	120.07	40	87	3.29	0.038	10.96	0.0030	0.132	0.092	0.94
2	»	100.06	50	113	5.36	0.048	11.02	0.0051	0.220	0.094	0.96
1	oligoclase	75.33	25	140	11.28	0.081	11.07	not determ.	—	—	—
5	»	75.66	25	144	14.10	0.098	11.09	»	»	—	—

**Microcline.** Table 2 gives the results of a number of experiments. The chemical decomposition of the feldspar seems to end when  $p_H$  10.7 is reached. During long rotations, therefore, a lower per cent of the disintegrated feldspar has been decomposed chemically than during the short rotations, as is shown in the table. Only small quantities of alkali were dissolved, the maximum being 0.26 % of the disintegrated feldspar. The experiments are arranged in the order of the quantities of mineral which were disintegrated, except the last two, which were carried out partly

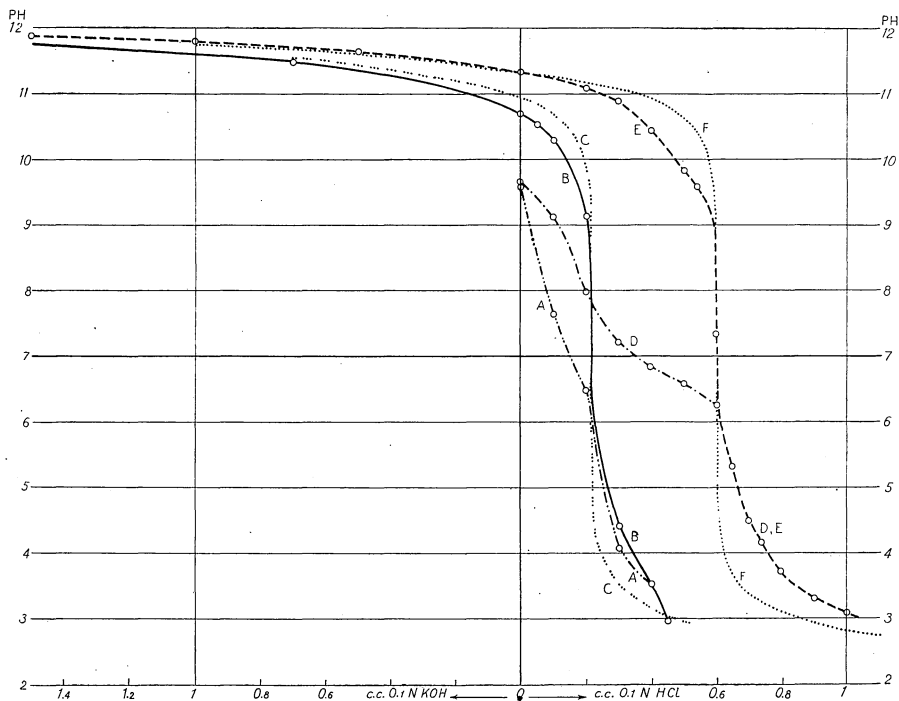


Fig. 2. Electrometrical titrations of ultrafiltrates of suspensions obtained in disintegrations. A: titration with 0.1 N HCl. B: back titration with 0.1 N KOH. C: back titration curve, calculated on the assumption that the original liquid was free from buffer substances; rotation experiment microcline 16. D: titration with HCl. E: back titration with KOH. F: calculated back titration curve; rotation experiment microcline 12.

for another purpose than the rest. The quantity of disintegrated mineral varies rather irregularly with the rotation time, owing to the predominant rôle played by the form of the feldspar fragments.

Fig. 2 gives the complete titration curves for the filtrates from two of the disintegration experiments, given in table 2. These curves show that not only alkali but also small quantities of substances which act as buffers between  $p_H$  3 and 6 as well as between  $p_H$  9 and 11.3 are found

in the solutions. This buffer effect is very probably caused by small amounts of aluminium ions (p. 13).

If the disintegration of the felspar takes place in an aqueous acid solution, the acid will be neutralized by alkali produced from the felspar. An experiment (microcline, No. 31) was carried out with 100.15 grams of felspar and 50 c. c. water + 2.0 c. c. 0.1 N HCl in a quartz glass cylinder for 210 hours. The result was 5.15 g. disintegrated felspar and the  $p_H$  of the liquid was 10.03. Another experiment (microcline, No. 33)

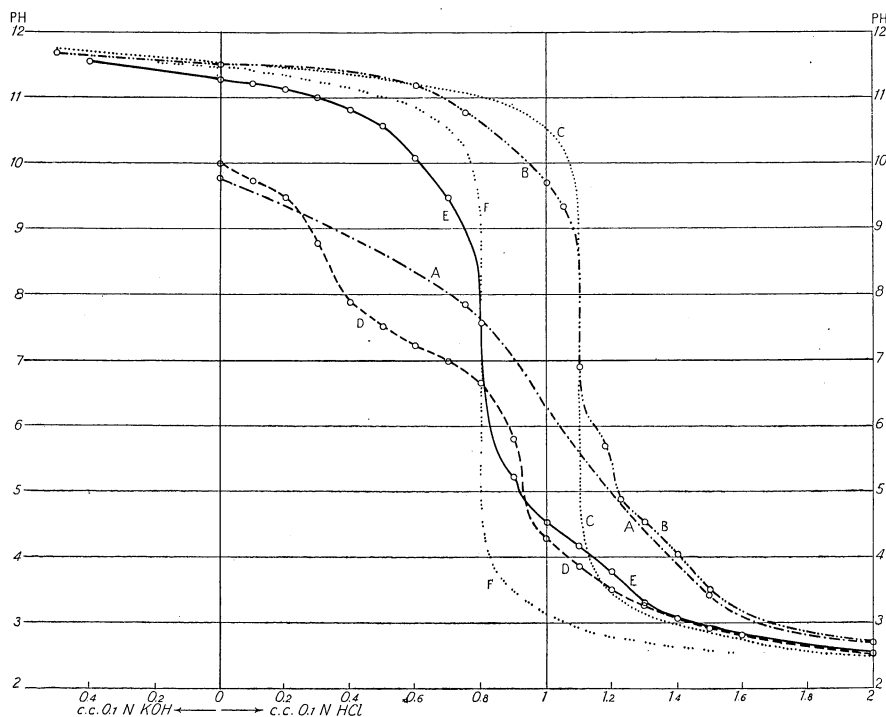


Fig. 3. Electrometric titration of ultrafiltrates of suspensions obtained in disintegrations. A: titration with 0.1 N HCl. B: back titration with 0.1 N KOH. C: back titration curve, calculated on the assumption that the original liquid was free from buffer substances; rotation experiment oligoclase 2. D: titration with HCl. E: back titration with KOH. F: calculated back titration curve; rotation experiment oligoclase 11.

with 97 g. felspar and 35 c. c. 0.001 N HCl for 65 hours gave 4.22 g. disintegrated felspar and a  $p_H$  of 10.46. Thus, the limiting alkalinity for the chemical decomposition of the felspar has been almost reached. An experiment (microcline, No. 22) with 100.08 g. felspar and 50 c. c. water, saturated with  $CO_2$  at the temperature of the room ( $p_H = 4$ ) gave, during 216 hours, 7.98 g. disintegrated felspar and a  $p_H$  of about 8.7.

**Oligoclase.** Table 3 gives the results of some experiments with

oligoclase. The chemical decomposition of that mineral seems to end at a  $p_H$  of 11.1, i. e. a higher value than that which was found in connexion with microcline. Fig. 3 shows the complete titration curves for the ultrafiltrates from two experiments with oligoclase. These curves resemble those of microcline. The filtrate from the disintegrated oligoclase also contains small quantities of substances that have a buffer action between  $p_H$  3 and 6 as well as between  $p_H$  8.5 and 11. In this case also the effect may be due to small quantities of Al ions (p. 19).

If the disintegration takes place in aqueous acid solutions, these will be neutralized. An experiment (oligoclase No. 12) with 75.11 g. oligoclase in the cylinder of the same material, and 25 c. c. 0.001 N HCl gave, in 65 hours, 2.04 g. of disintegrated feldspar and a  $p_H$  of 9.57. Another experiment (oligoclase No. 8) with 75.92 g. oligoclase in the cylinder of the same material and 40 c. c. water + 1.0 c. c. 0.1 N HCl gave, in 125 hours, 25.90 g. disintegrated feldspar and a  $p_H$  of 10.04. The exceptionally large amount of feldspar which was disintegrated is explained by the fact that sharply edged pieces were used in this experiment. Another experiment (oligoclase No. 4) with 75 g. oligoclase and 40 c. c.  $H_2O$  + 10 c. c. 0.1 N HCl in the oligoclase cylinder for 410 hours gave 10 g. disintegrated feldspar and a  $p_H$  of 9.43. A last experiment with 75.08 g. oligoclase and 25 c. c.  $H_2O$  + 1.0 c. c. 0.1 N HCl gave, in 120 hours, 3.64 g. of disintegrated feldspar and a  $p_H$  of 10.65.

The disintegration of microcline and oligoclase in water leads to a chemical decomposition of the minerals, which yields free alkali ions, and therefore rapidly raises the  $p_H$  of the liquid up to a certain limit (approx. 10.7 and 11.1). Practically the whole process will thus take place in an alkaline medium. If the grinding takes place in an aqueous solution of an acid, this will be neutralized by alkali from the feldspar.

### The Reactions of the Feldspar Particles with H-ions.

**Microcline.** Two rotation experiments, microcline No. 13 and 30 (table 2), were chosen for investigation. These were carried out in exactly the same way. The particles, which were obtained during the disintegration, were suspended in a volume of water, which was chosen so that 25 c. c. contained 0.50 g. feldspar particles. In experiment 13 the particles were first separated from the rotation liquid by ultrafiltration. They contained therefore traces of  $CO_2$ , which they might have absorbed from the air during this operation. In experiment 30 the suspension, which was formed during the disintegration, was used directly. It was diluted

with pure water, and the concentration was regulated with the aid of analyses. 10 c. c. of the suspension contained a residue of 0.2211 g. after evaporation and drying in vacuo over concentrated sulphuric acid at room temperature. After drying in air at a temperature of  $105^{\circ}$ — $110^{\circ}$  C the residue weighed 0.2204 g. After heating to the temperature of dark red-glowing the weight was 0.2178 g. The residue thus contained 1.18 per cent. water. By calculating the weights of the felspar pieces and the cylinder before and after the disintegration, the figures 0.200 g. felspar and 0.018 g. quartz glass, i. e. 0.218 g. in all in 10 c. c.,

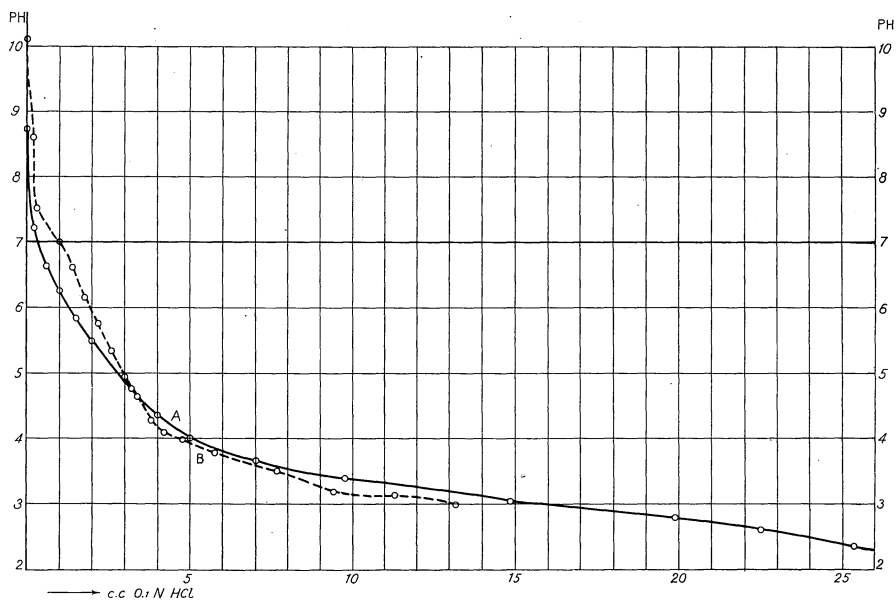


Fig. 4. Consumption of HCl per gram of felspar particles at different  $p_H$  values, according to electrometric titrations at 3 minute intervals. A: rotation experiment microcline 13. B: rotation experiment microcline 30.

were obtained. The agreement between the found and the calculated quantities is very good, and it is therefore permissible to calculate the concentrations of the rotation-liquids from the losses in weight of the felspar pieces and of the cylinder employed. Thus 25 c. c. contained 0.50 g. felspar particles and 0.044 g. quartz glass particles. In experiment 13, 25 c. c. contained 0.50 g. felspar particles and 0.087 g. quartz glass particles.

25 c. c. of the above suspensions were titrated electrometrically with 0.1 N HCl. The titrations were carried out in the manner already described. The result is given in fig. 4, which shows the quantities of HCl neutralized by the particles at different  $p_H$ -values. In experiment 30,

a small quantity of alkali from the rotation decomposition must have contributed to the neutralization of the HCl. This quantity was calculated from the titration curve for the ultrafiltrate from the identical experiment No. 13 (table 2) and subtracted. The two curves in fig. 4 are thus quite comparable.

The results of the two experiments 13 and 30 agree very well. In No. 30, where the liquid was free from  $\text{CO}_2$ , the  $p_{\text{H}}$ -value, before the titration, was higher than in No. 13. The titrations were carried out at regular intervals, as described on p. 7. This is necessary, because the reaction between the particles and the H-ions will continue slowly for an appreciable time. Another titration was made on 25 c. c. of the suspension from experiment No. 13 to determine the whole quantity of HCl which would react with the particles at a  $p_{\text{H}}$  of 3.00, over a long time interval. After adding 8.0 c. c. 0.1 N HCl the  $p_{\text{H}}$  of the liquid was 3.00. The liquid was then shaken, and the  $p_{\text{H}}$  rose to 3.48. It was titrated again to  $p_{\text{H}}$  3.00, shaken, titrated to  $p_{\text{H}}$  3.00 once more, and so on. It is difficult to determine exactly the end point of the reaction between HCl and the particles. The process bears a similarity to natural weathering in an acid medium. Over a long time it is probable that large quantities of the particles would react. In the operations described 19.06 c. c. 0.1 N HCl per gram felspar particles were consumed in 5 days. After this the  $p_{\text{H}}$  of the liquid rose only slightly when it was shaken.

It is very probable that the felspar is completely decomposed by the acid (see further on) whereby the alkali as well as the aluminium is neutralized when  $p_{\text{H}}$  3 is reached. Felspar contains 3 equivalents of Al to 1 equivalent of K (or Na, Ca). If the consumption of HCl per gram of felspar is considered to be distributed in these proportions between alkali and aluminium, the quantities of alkali and aluminium ions in the liquid can be calculated from the total consumption of HCl. Thus, 19.06 c. c. 0.1 N HCl equals 1.43 milli-equivalents of Al and 0.476 m. e. of K (or Na). After the titration the suspension was ultrafiltered, and the filtrate was analysed for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . It contained 0.0037 g.  $\text{SiO}_2$  and 0.0119 g.  $\text{Al}_2\text{O}_3$ , the latter figure corresponding to 1.40 milli-equivalents Al per gram felspar particles. The accordance between the aluminium value, calculated from the HCl consumption, and the analytically determined quantity is very good.

The microcline contains about 11.40 milli-equivalents of aluminium per gram. The figure is calculated as an average of the analyses on p. 2. Thus the HCl has decomposed 12—13 % of the mineral at a  $p_{\text{H}}$  of 3.00. If we consider the curves in fig. 4, we find in the same way that 8—9 %



and 10—11 % respectively of the felspar is decomposed, when  $p_H$  3 is reached.

For the further study of the decomposition of the felspar particles, 25 c. c. from rotation experiment No. 13 was titrated with 0.1 N HCl to  $p_H$  2.40. The titration took 14 c. c. HCl. By means of a rapid stream of hydrogen all traces of  $CO_2$  were removed from the liquid, which was then ultrafiltered. The  $p_H$  of the filtrate was 2.52. 26 c. c. of it was

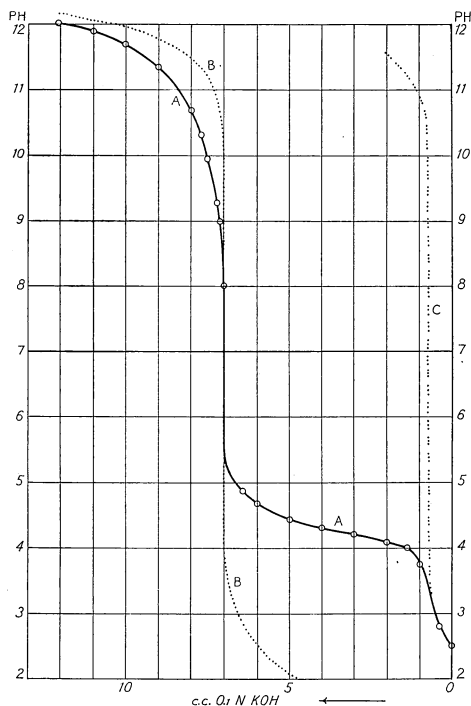


Fig. 5. Electrometric titration with 0.1 N KOH of ultrafiltrate from felspar particles which had been titrated with HCl to  $p_H$  2.40. A: titration curve. B and C: titration curves, calculated on the assumption that the liquid was free from buffer substances. Rotation experiment microcline 13.

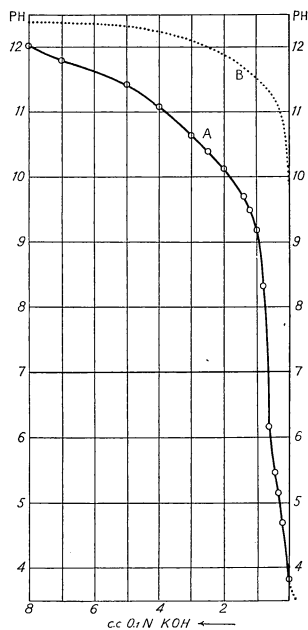


Fig. 6. Electrometrical titration of filter residue from same operation as in fig. 5. A: titration with 0.1 N KOH. B: titration curve, calculated on the assumption that the liquid was free of buffer substances. Rotation experiment microcline 13.

titrated with 0.1 N KOH to  $p_H$  12. The curve obtained is given in fig. 5. It shows a strong buffer action between  $p_H$  3.5—5.5 as well as a lesser one between  $p_H$  8.5—12. This buffer action is undoubtedly due to aluminium. The particles retained by the filter were suspended in 25 c. c. of water and titrated electrometrically with 0.1 N KOH. The titration curve is given in fig. 6. The buffer action is rather weak between  $p_H$  4—6, but strong between  $p_H$  8.5—12. Thus, the strong buffer action

in the acid range of a suspension of felspar particles, which have not been ultrafiltered (see further, fig. 7), is confined to aluminium.

As a consequence of these results, it is evident that the reaction of the felspar particles with H-ions in the  $p_H$ -range, which was examined, is not reversible, i. e. it is not merely an ion exchange. This is also evident from fig. 7, which gives the complete titration curve for a suspension of felspar particles, without  $\text{CO}_2$  (rotation experiment microcline No. 11).

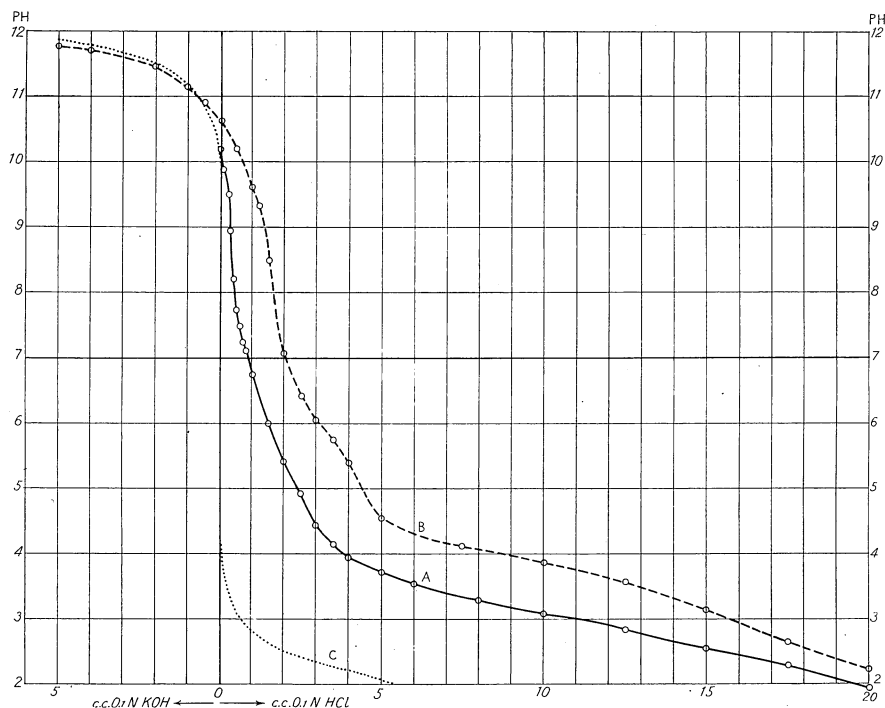


Fig. 7. Rotation experiment microcline 11. 0.65 g. microcline particles in 25 c.c. water. A: titration with 0.1 N HCl. B: back titration (after 30 minutes) with 0.1 N KOH. C: back titration with 0.1 N KOH calculated for a liquid consisting of 25 c.c.  $\text{H}_2\text{O}$  + 20 c.c. 0.1 N HCl.

25 c.c. of the suspension, containing 0.65 gram of felspar particles together with an amount of alkali, corresponding to 0.13 c.c. 0.1 N HCl, was titrated with HCl to  $p_H$  2.0. After 30 minutes the  $p_H$  had risen to 2.22. The liquid was now titrated back with 0.1 N KOH to  $p_H$  11.77. It may be observed that the titration curve between  $p_H$  11 and 12 follows the curve, which was obtained by calculating the titration curve of the same volume of water. Thus, in that  $p_H$ -range there is no buffer action, i. e. the felspar particles do not react with the

water solution. This is in accordance with the fact that the chemical decomposition during the rotations comes to a stop, when  $p_H$  10—11 is reached (table 2).

However, it is possible that the felspar particles do react in another way (e. g. by ion exchange) in a  $p_H$ -range, where Al does not form simple ions. To elucidate this question, 25 c. c. of the suspension from experiment 30, containing 0.50 g. felspar particles, was ultrafiltered and immediately suspended in 25 c. c.  $CO_2$ -free water in an electrode vessel in a stream of hydrogen. The  $p_H$  was determined, and then the liquid was titrated with 0.1 N HCl to a  $p_H$  of about 6. The solution was

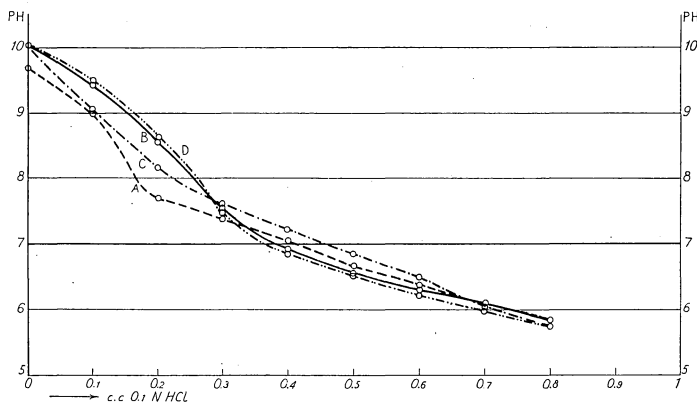


Fig. 8. Rotation experiment microcline 30. Electrometric titration of 0.50 g. microcline particles in 25 c. c.  $H_2O$ . A: titration with 0.1 N HCl. B: back titration with 0.1 N KOH. C: re-titration with 0.1 N HCl. D: back titration with 0.1 N KOH.

immediately titrated back with an equal quantity of 0.1 N KOH. Once more it was immediately titrated with the same quantity 0.1 N HCl and back with 0.1 N KOH. The titration curves are given in Fig. 8. They show clearly that the reaction between the particles and H-ions is reversible and consequently essentially an ion exchange. At  $p_H$  6, 4.2 % of the felspar particles have been decomposed by ion exchange.

In the  $p_H$ -range 10.5—6 the felspar particles exchange their alkali ions in a reversible way with hydrogen ions. In the range 6—3 an irreversible decomposition takes place, which destroys the space lattice of the felspar with the liberation of free aluminium ions. It was found that 12—13 % of the particles could be decomposed in such a way.

**Oligoclase.** The results of the two rotation experiments oligoclase

No. 1 and No. 10 were chosen for investigation. It should be mentioned that in experiment No. 10 the felspar fragments were very rounded, and hence only a very small amount of particles was obtained. The particles must, however, have been very finely divided. Thus they contained 3.30 % of water, either after drying over concentrated sulphuric acid in vacuo at room temperature, or after drying at a temperature of  $105^{\circ}$ — $110^{\circ}$  C in air. In experiment No. 1, the pieces were edged, and a

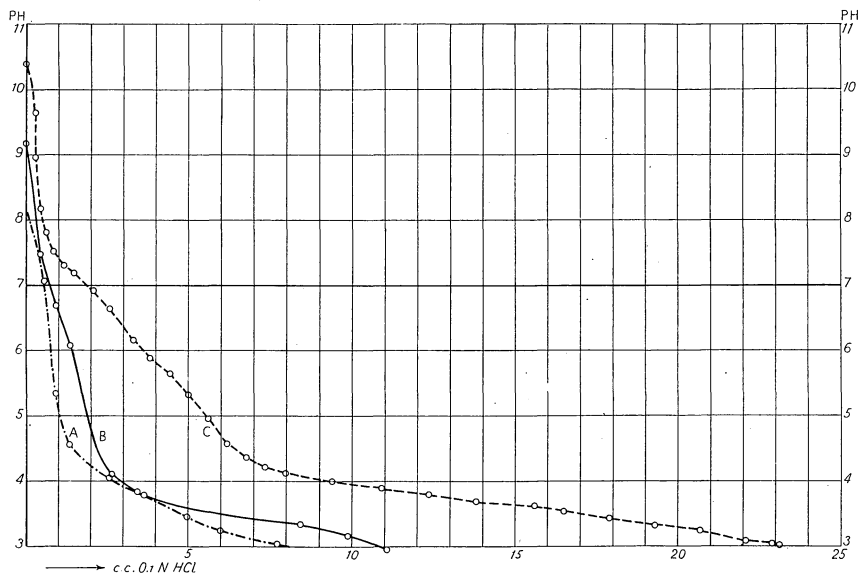


Fig. 9. Consumption of HCl per g. felspar particles at different  $p_H$ -values, according to electrometric titration at 3 minute intervals. A: rotation experiment oligoclase 1. B: rotation experiment oligoclase 1, the titration carried out somewhat differently from A. C: rotation experiment oligoclase 10.

larger quantity of particles was obtained, which contained only 1.60 % of water. Experiment No. 1 as well as No. 10 are included in table 3, p. 8.

The particles from both experiments were titrated electrometrically in the following way: No. 1. 5 c. c. suspension, containing 0.225 g. felspar particles, was rapidly ultrafiltered and the particles suspended in 25 c. c.  $\text{CO}_2$ -free water in the electrode vessel, through which a current of hydrogen was passing. The  $p_H$  was determined, and the liquid was titrated with 0.1 N HCl to  $p_H$  3. — No. 10. 25 c. c. of the suspension, which was formed during the rotation, was immediately introduced into the electrode vessel, through which a stream of hydrogen was passing, and titrated. Another 20 c. c. of the suspension was ultrafiltered, and the ultrafiltrate was titrated electrometrically, whereby the HCl-consump-

tion of the alkali dissolved during the rotation was determined. The particles on the filter were weighed, and their water content was determined. The concentration of the titrated suspension was thus known, and a correction was made for the HCl consumed by the alkali dissolved during the rotation.

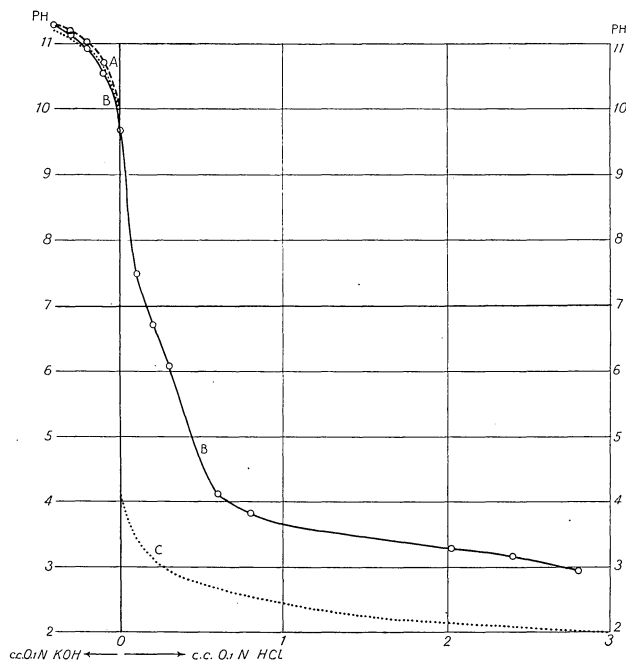


Fig. 10. Electrometric titration of 0.225 g. ultrafiltered oligoclase particles in 25 c. c.  $\text{CO}_2$ -free water. A: titration with 0.1 N KOH. B: titration with 0.1 N HCl. C: titration curve, calculated on the assumption that the liquid was free of buffer substances. Rotation experiment oligoclase 1.

Fig. 9 gives the HCl consumption of the oligoclase particles. The finely divided particles of experiment No. 10 were much more decomposed chemically than those of the other. The curves closely resemble those from microcline (fig. 4). When the liquid was shaken after  $p_H$  3.00 had been reached, the  $p_H$  rose slowly and a fresh quantity of HCl had to be used to bring the  $p_H$  back to 3.00 again. As in the case of microcline, it is difficult to determine the end point of the reaction at  $p_H$  3.00. It is a weathering process. During 3 days the particles from No. 1 thus consumed 17.1 c. c. 0.1 N HCl per gram, the particles from No. 10 29.60 c. c. (including the first consumption in the  $p_H$ -range 11—3).

Fig. 10 shows another titration of 0.225 g. oligoclase particles in 25 c. c.

pure ( $\text{CO}_2$ -free) water, rotation experiment No. 1. The suspension was first titrated with 0.1 N KOH, giving a curve that closely approximates to the curve calculated for the same volume of pure water. Thus, the particles do not react with the liquid in the  $p_{\text{H}}$ -range 10—11.3. This fact agrees with the result from microcline particles (fig. 7, p. 15). In tables 2 and 3, it is shown that the decomposition of feldspar by water ceases at a  $p_{\text{H}}$  of 10.7—11.1. This, too, is in accordance with what has just been described. There is perhaps an equilibrium between the silicate and the hydrogen

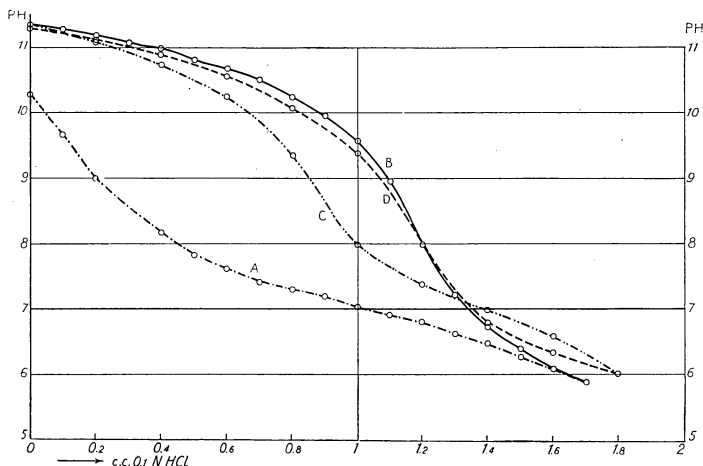


Fig. 11. Rotation experiment oligoclase 5. Electrometric titration of 0.936 g. oligoclase particles in 25 c. c.  $\text{CO}_2$ -free water. A: titration with 0.1 N HCl. B: back titration with 0.1 N KOH. C: re-titration with 0.1 N HCl. D: back titration with 0.1 N KOH.

ions. This question, however, cannot be settled without further investigations.

The oligoclase particles like the microcline, are also decomposed by hydrogen ions with liberation of aluminium ions. The following experiment brings out this clearly. 25 c. c. of a suspension of 0.52 g. oligoclase particles (from rotation experiment oligoclase No. 1, with no particles  $> 2 \mu$ , p 6) was titrated with 0.1 N HCl to  $p_{\text{H}}$  3.00. The particles consumed 14.90 c. c. HCl per gram. This consumption can be considered to be distributed between alkali and aluminium in the proportion 1 : 3. Three quarters of the HCl used corresponds with 1.12 milli-equivalents of Al ions per gram of particles. After titration, the liquid was ultrafiltered and analysed. It contained 0.56 g.  $\text{SiO}_2$  and 0.0106 g.  $\text{Al}_2\text{O}_3$ , equal to 1.20 milli-equivalents of Al per gram of particles. The agreement is quite satisfactory. The feldspar contains 13.70 milli-equivalents of Al per gram (calculated from the average composition, p. 2). Thus, about

8—9 % of the oligoclase has been decomposed chemically. This is less than what was formed in connexion with microcline, (p. 13). In the case of microcline, however, the titration with HCl had been continued during several days. Thus, the two results are not wholly comparable. From the results given in fig. 9, it can be calculated that in the case of No. 1, 9—10 %, and in the case of No. 10, 16—17 % of the particles were decomposed at a  $p_H$  of 3.00. Hydrogen ions thus have about the same decomposing power on oligoclase as on microcline.

The reaction of oligoclase with hydrogen ions was also investigated between  $p_H$  11 and  $p_H$  6, within which range aluminium does not ionise.

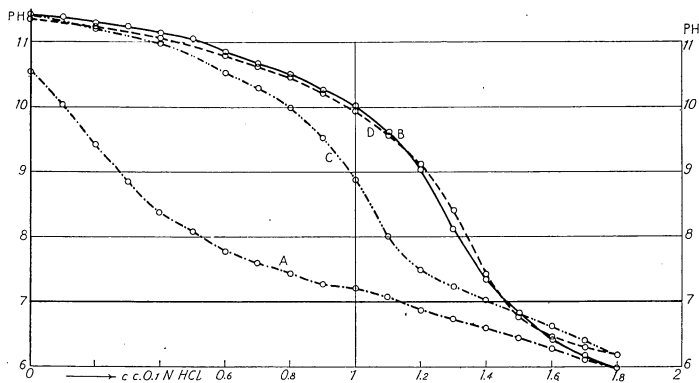


Fig. 12. Rotation experiment oligoclase 5. Electrometric titration of 0.936 g. oligoclase particles in 25 c. c.  $CO_2$ -free water. A: titration with 0.1 N HCl. B: back titration with 0.1 N NaOH. C: re-titration with 0.1 N HCl. D: back titration with 0.1 N NaOH.

10 c. c. of a suspension, containing 0.9364 g. particles from rotation experiment oligoclase No. 5 was rapidly ultrafiltered and the particles suspended in 25 c. c. of pure water in the electrode vessel in a stream of hydrogen. The  $p_H$  was determined and the liquid then titrated in the same way as has been described in connexion with microcline (p. 16). The results are given in fig. 11. It should be mentioned that the quantity of particles titrated was about double the quantity used in the microcline titration. The scale of fig. 11, however, is half of that of fig. 8, so that the two are directly comparable. The oligoclase particles contained 1.36 % water, determined in the way described above.

Fig. 11 shows an entirely different state of affairs from that of fig. 8. The oligoclase particles are not capable of reversible ion exchange in the same way as the microcline particles. However, the diverse results might perhaps be explained by the fact that the titration in fig. 11 was made with HCl and the corresponding quantity of potassium hydroxide. There-

fore another titration was carried out with 0.1 N HCl and 0.1 N NaOH, but otherwise in exactly the same way. The result of that titration is given in fig. 12. It accords very well with the result in fig. 11. From fig. 11 and 12 the quantity of disintegrated feldspar decomposed chemically at  $p_H$  6 was calculated to be 4.2 %, the same percentage as was found in connexion with microcline.

The oligoclase particles reacted irreversibly with hydrogen ions in the whole  $p_H$ -range 11—3. In the  $p_H$ -range 6—3 the aluminium of the mineral was transformed into ions. At  $p_H$  3.00 9—17 % of the particles were decomposed by hydrogen ions. There is a great difference in the behaviour of the microcline and the oligoclase in the  $p_H$ -range 11—6; the former reacts reversibly, the latter does not. This easily accounted for if the microcline particles like many natural weathering products of potash feldspar, contain muscovite particles, which themselves exhibit ion exchange. The natural weathering of plagioclase does not give rise to mica particles, which exhibit ion exchange.

### Rotation Experiments in Acid Water Solutions.

Some experiments were carried out in the following way: 100 g. feldspar pieces and 50 c.c. 0.001 N HCl ( $p_H = 3.00$ ) were agitated in a quartz glass cylinder for an hour, and the  $p_H$  of the liquid in the cylinder was then determined. It was generally about 4, or somewhat higher. The liquid was titrated electrometrically with 0.1 N HCl to  $p_H = 3.00$ , and then poured back into the cylinder. The same operations, shaking,  $p_H$ -determination and titration to  $p_H = 3.00$  were repeated several times. The times of shaking between the titrations were, however, gradually increased, which could be done without the liquid becoming less acid than  $p_H$  4. After several hours agitation, the liquid was titrated with 0.1 N HCl to  $p_H$  3.00 and by repeated titrations was kept at this  $p_H$ -value for some days. By weighing the feldspar pieces before and after the rotations the quantity of feldspar particles formed was determined.

1. **Rotation experiment, microcline No. 19.** The whole rotation time was 7 hours, the quantity of feldspar disintegrated 0.16 g. After the first hour the  $p_H$  was 4.40, after which 4 was not exceeded. 3.03 c.c. 0.1 N HCl was consumed by the particles formed, corresponding to 19 c.c. per gram.

2. **Rotation experiment, microcline No. 21.** The whole rotation time was 51.5 hours, and 1.43 grams of feldspar were disintegrated. The



$p_H$  never rose above 4.11, the value reached after the first hour's shaking. 27.22 c. c. 0.1 N HCl was consumed in the titration, corresponding to 19.25 c. c. per gram of particles, in good agreement with the previous experiment.

3. **Rotation experiment, oligoclase No. 9.** The whole rotation time was 13 hours, and 1.20 g. oligoclase was disintegrated. In the first hour, the  $p_H$  reached 5.20, afterwards 4 was not exceeded. 16.68 c. c. 0.1 N HCl was consumed, corresponding to 13.9 c. c. per gram of disintegrated felspar.

It follows from the above experiments that the HCl consumption per gram of disintegrated felspar is of the same order as in the experiments in which the felspar was disintegrated in alkaline water and afterwards titrated with HCl. Thus, in rotation experiment, microcline No. 13, (p. 13), there was a consumption of 19.06 c. c. 0.1 N HCl, a really remarkable agreement. The oligoclase particles from rotation experiment, oligoclase No. 1 (p. 18), consumed 17.1 c. c. 0.1 N HCl per gram. Full agreement cannot be expected, since the chemical processes depend on the size of the particles, which in its turn is partly dependant on the shape of the felspar fragments. Nevertheless, the above experiments indicate that approximately the same result is obtained whether the felspar is disintegrated in alkaline solution ( $p_H$  9—11) and afterwards exposed to the attack of hydrogen ions, or if it is directly disintegrated in acid solution ( $p_H$  3—4).

When felspar was disintegrated at  $p_H$  4—3, the particles formed consumed about as much of hydrogen ions as when the disintegration took place in alkaline water and the particles afterwards were brought to react with H-ions until  $p_H$  3.00 was reached.

### Titration of Particles of Different Size.

On pp. 4—7, the fractionation of felspar particles has been described. The fractions obtained were titrated with 0.1 N HCl. A part of each fraction was ultrafiltered, the residue on the filter was immediately introduced into 25 c. c.  $CO_2$ -free water in the electrode vessel through which a stream of hydrogen was passing. The  $p_H$  was determined and the liquid titrated with 0.1 N HCl to  $p_H = 3.00$ . Additional quantities of HCl were added at intervals in the course of at least two days, so as to keep the  $p_H$  at 3, and thereby to determine the total HCl consumption of the particles at this  $p_H$ .

The results obtained with microcline are given in Fig. 13. The different fractions are denoted by the same letters, A, B, D as on p. 5.

A is the finest fraction, It is clear that the size plays a very important rôle in the reaction between the particles and hydrogen ions. If we compare the HCl consumptions of the different fractions with that of the unseparated suspension (fig. 4 p. 12, No. 13), we find that the latter lies between A and B. The smallest particles ( $0.47 \mu$ ) consume much more HCl than the others. During the following days fraction B ( $0.82 \mu$ ) consumed a further 6.43 c. c. 0.1 N HCl per gram of particles, i. e. 98 % of its previous consumption. Fraction A ( $0.47 \mu$ ), however, consumed only 5.2 c. c. per gram or 21 % of its previous consumption. After 6 days more a further 4.9 c. c. per gram had been consumed, making

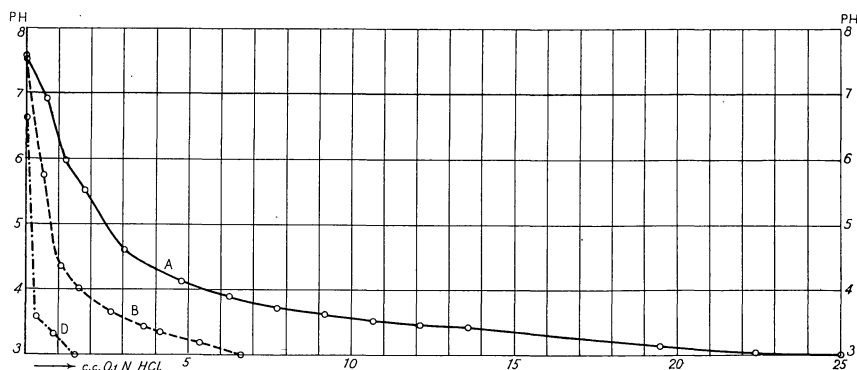


Fig. 13. Consumption of 0.1 N HCl per g. feldspar particles of different known sizes. A: particles of average diameter  $0.47 \mu$ . B:  $0.82 \mu$ . D:  $> 2 \mu$ . Rotation experiment microcline 13. Cp fig. 4, A.

a total of 41 % of the previous consumption. Thus, the very small particles react rapidly at first, and afterwards undergo relatively little decomposition if the  $p_H$  is kept at 3.00. The larger particles, on the other hand, react slowly on the first titration, but afterwards undergo relatively more decomposition than the smaller particles under similar conditions ( $p_H = 3$ ).

In the same way as on p. 13 it can be calculated that 8.5 % of fraction B and 23.0 % of fraction A had been decomposed by the hydrogen ions. It should be noted, however, that the two fractions B and A contained some quartz particles (table 2), and it is not known in what proportions these were distributed among the different fractions.

Fig. 14 gives the results obtained with oligoclase. The different fractions (p. 6) consumed very different amounts of 0.1 N HCl per gram. Here the particles consisted of feldspar products only, as the disintegration was made in the oligoclase cylinder. The HCl consumption of the unfractionated suspension of oligoclase particles is given in fig. 9 p. 17, No. 1. It agrees approximately with fraction E ( $0.57 \mu$ ). Five days

after the titration, the consumption of HCl was determined at  $p_H = 3.00$  in the way described above. Fraction A ( $0.44 \mu$ ) had increased its HCl consumption from 18.4 c. c. to 26.2 c. c. per gram of particles, i. e. by 42 %. For fraction E ( $0.57 \mu$ ) the corresponding values were 8.1, 14.6 and 83 % and for fraction F ( $1.06 \mu$ ) 4.8, 9.6, and 100 %. The finest particles are thus more rapidly attacked by the acid and afterwards undergo less decomposition at  $p_H = 3.00$  than the coarser particles, an entirely analogous result to that obtained with microcline. According to the method given on pp. 19—20, it can be calculated that of fraction A, 14.4 %, of E, 7.6 %, and of F, 5.0 % was decomposed by hydrogen ions.

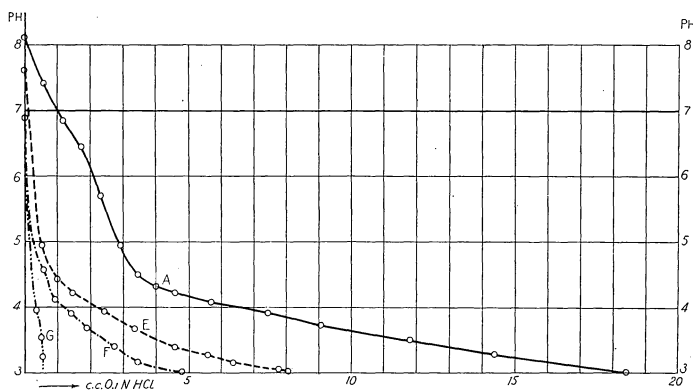


Fig. 14. Consumption of 0.1 N HCl per g. felspar particles of different known sizes. A: particles of average diameter  $0.44 \mu$ . E:  $0.57 \mu$ . F:  $1.06 \mu$ . G:  $> 2 \mu$ . Rotation experiment oligoclase 1. Cp. fig. 9, A and B.

The decomposition of felspar particles by hydrogen ions depends in a high degree on the size of the particles. If they are greater than  $2 \mu$ , they are only slightly attacked. If their average size is  $0.4 \mu$ — $0.5 \mu$ , a large part of them is decomposed chemically by hydrogen ions; e. g., at a  $p_H$  of 3.00, 14—23 % was found to be decomposed. Among the particles of average size  $0.4 \mu$ — $0.5 \mu$ , there is probably a number of smaller ones that are completely decomposed.

## Summary.

1. Hard minerals were disintegrated into particles of dimensions  $2 \mu$ — $0.2 \mu$  by the self-grinding of mineral fragments in water. By this means silicate minerals can be subdivided into the dimensions that are characteristic of clays. The method appears to be generally applicable to hard substances,

such as metals (e. g. silver) or quartz which, provided they are not attacked by water, can thus be obtained in colloidal solution. It can be used in the chemical study of clay formation and chemical weathering, as well as in the field of colloid chemistry.

2. With the help of the above method of disintegration, some tentative investigations have been made into the processes of clay formation and the weathering of feldspars. When a feldspar is disintegrated in pure water, a small part is rapidly decomposed, and the water becomes alkaline. This decomposition, however, seems to stop when a  $p_H$  of 10.7 is reached in the case of microcline, or a  $p_H$  of 11.1 in the case of oligoclase. The products of disintegration take up appreciable amounts of water, the amounts increasing with the fineness of division of the particles. This water is not driven off by drying in vacuo over sulphuric acid at room temperature, nor by heating in air to  $105^{\circ}$ — $110^{\circ}$  C. When acids are present during the disintegration, they are neutralized until the limiting  $p_H$ , at which the feldspar is no longer affected, is reached.

3. The particles prepared from feldspars react readily with hydrogen ions. Within the  $p_H$ -range 10—6 the reaction with microcline particles appears to be one of base exchange, in which hydrogen ions are reversibly absorbed by the particles. This recalls the property possessed by muscovite particles, which are often formed in nature by the weathering of potash feldspar, of exchanging potassium and hydrogen ions. Oligoclase, on the other hand, is decomposed irreversibly within the  $p_H$ -range 10—6. There is thus here a definite chemical difference between oligoclase and microcline. This difference finds its parallel in natural weathering, for plagioclase is not converted into mica in the same way as potash feldspar.

Within the  $p_H$ -range 6—3 a more pronounced decomposition of the feldspar particles takes place with liberation not only of alkali, but also of aluminium ions. In one case investigated up to 17 % of the particles had been decomposed. This decomposition also has a close parallel in nature. In strongly acid soils, such as are found under raw humus in coniferous forests, a  $p_H$  of 3.8—4 prevails (HESSELMAN 1926). In such soils the feldspars weather without leaving any aluminium-rich residue (TAMM 1915, p. 193, 1920, p. 283). Under other conditions kaolin-like substances are produced from the feldspars. It seems probable that the formation of kaolin (or kaolin-like substances) is a weathering process that requires a  $p_H$  of 6—11 for its accomplishment. This affords a simple explanation why the weathering of feldspar gives rise to kaolin in some cases, but not in others.

4. If the disintegration takes place in an acid solution, the products seem to be decomposed chemically to the same extent as if the disintegration had first been effected in an alkaline solution, and the products then treated with an acid.

5. Felspar particles of dimension  $0.2\ \mu$ — $0.5\ \mu$  readily react with hydrogen ions with the simultaneous liberation of bases. But if the size of the particles is greater than  $2\ \mu$ , they are not appreciably attacked. This result has a certain interest from the point of view of plant physiology. It indicates the dimensions that a mineral particle should have, to be able readily to give up its valuable constituents. It would be interesting (and, technically, not difficult) to carry out plant growth experiments with freshly prepared disintegration products of feldspars and other minerals. The fact has also some bearing on soil analyses. Analytical dates of a soil rich in clay particles smaller than  $2\ \mu$  are clearly not very reliable if they have been obtained by extraction of the soil with an acid liquid. Such one does attack small particles of common soil minerals.

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## SAMMANFATTNING.

### En experimentell studie över lerbildning och vittring av fältspater.

**Förord.** År 1927 började förf. en experimentell undersökning över silikatisk vittring och erhöill i samband därmed ett understöd av Kgl. Svenska Vetenskapsakademien ur LETTERSTEDT'ska fonden för att möjliggöra anskaffandet av diverse behövlige apparater. Sedermera, 1928, erhöill jag ett resestipendium från International Education Board (ROCKEFELLER stiftelsen) som satte mig i stånd att vistas omkring fem månader i Köpenhamn hos professor N. BJERRUM på den Kgl. Veterinær- og Landbohøjskoles kemiske Laboratorium, där nedan beskrivna undersökning utförts under Professor B:s ledning. Ehuru arbetet från början ej föll inom Statens Skogsförsöksanstalts arbetsprogram har professor HESSELMAN tillåtit mig att publicera detsamma i Meddelanden från Statens Skogsförsöksanstalt.

Till alla, såväl institutioner som enskilda, vilka på ett eller annat sätt varit mig behjälpliga vid fullföljandet av min undersökning ber jag att få rikta ett vördsamt och varmt tack. Särskilt ber jag därvid att få vända mig till professor BJERRUM.

Den Kgl. Veterinær- og Landbohøjskole, Köpenhamn, i juli 1928. O. TAMM

**Inledning.** För femtio år sedan utförde den franske geologen A. DAUBRÉE (1879) ett experiment för att studera lerbildning och vittring av fältspat. Han lät stycken av ortoklas rotera med vatten i en cylinder av järn under 192 timmar. Fältspaten maldes därvid till stor del sönder till slam och betydande mängder kali gingo i lösning. Senare har jag använt D:s metod för att studera lerbildning av granit och granitmineral (1925, 1928). Emellertid borde metoden vara ägnad att i förening med moderna fysikalisk-kemiska metoder möjliggöra ett närmare studium av silikatmineralens kemiska egenskaper. Den här föreliggande undersökningen är ett första försök i denna riktning.

**Undersökta mineral.** Till experimenten användes tvänne markmineral, mikroklin (kalifältspat) och oligoklas (natronrik kalk-natronfältspat), båda från Ytterby, Stockholms län. Bägge äro ytterst vanliga i skogsmarken, där det förra är det kanske viktigaste bland kali-rika mineral och det senare ett betydelsefullt kalcium-mineral.

**Desintegrationsmetodik m. m.** Mineralstycken av 5—15 mm:s längd inneslötos med rent eller i vissa fall surgjort vatten i cylindrar av resp. kvarts-glans, rent silver eller oligoklas. I dessa cylindrar fingo fältspatstyckena rotera med kolsyrefritt rent vatten under olika tidsperioder, från några få till inemot 500 timmar. Härvid uppstår en lersuspension, varjämte en del av fältspaten sönderdelas kemiskt, så att vätskan kommer att innehålla basjoner. Genom sedimentering av lersuspensioner jämte centrifugering, uppdelades de bildade lerpartiklarna i fraktioner av olika kornstorlek, vilka undersöktes medelst ultramikroskop. Det visade sig att den allra största delen av de bildade partiklarna i storlek ligga mellan 0.2  $\mu$  och 2  $\mu$ . Partiklarna upptaga vid desintegrationen icke obetydliga mängder vatten.

**Kemiska processer under desintegrationen.** Genom ultrafiltrering av de vid desintegrationsförsöken i rent vatten erhållna suspensionerna, sedan

$p_H$  bestämts, och genom elektrometrisk titrering av de på så sätt erhållna lösningarna bestämdes den mängd baser, som gått i lösning. Härav beräknas att högst 1.87 % av den desintegrerade fältspatmängden sönderdelats kemiskt. Suspensionernas  $p_H$  överskred ej 10.7 (mikroclin) och 11.1 (oligoklas). Om vattnet i cylindern blivit försatt med en syra, neutraliseras denna och betydligt mer av fältspaten sönderdelas än i rent vatten.

**Fältspatpartiklarnas reaktioner med vätejoner.** Dessa reaktioner studerades medelst elektrometriska titreringar av partikelsuspensioner. Det visade sig att partiklarna till betydande grad sönderdelas av vätejoner, varvid vid  $p_H$  6—3 utom basjoner även aluminiumjoner gå i lösning. Här sker sålunda ett fullständigt sönderfall av silikatet till mer eller mindre lösliga beståndsdelar. Processen liknar mycket en vittringsprocess i naturen i surt medium. I  $p_H$ -området 10—6 är sönderdelningen mindre och leder ej till frigörande av aluminiumjoner. I fråga om mikroclin är den reversibel, d. v. s. mineralpartiklarna leverera kalium-joner i utbyte mot väte-joner. I fråga om oligoklas är sönderdelningen även mellan  $p_H$  10 och  $p_H$  6 irreversibel. Det föreligger sålunda härutinnan en kemisk olikhet mellan mikroclin och oligoklas. I  $p_H$ -området 10—6 erhöles i de undersökta fallen en kemisk sönderdelning av omkring 4 % av den desintegrerade fältspaten. Vid  $p_H = 3$  hade 8—17 % av densamma sönderdelats.

**Desintegration av fältspater vid  $p_H$  4—3.** När mikroclin och oligoklas desintegrerades i vatten, som med hjälp av successiva saltsyretillsatser hölls vid  $p_H = 4—3$  med slutlig titrering till 3, sönderdelades de kemiskt i ungefär samma omfattning, som när desintegrationen utfördes i rent vatten och dess produkt sedan behandlades med saltsyra intill  $p_H = 3$  uppnåddes.

**Elektrometrisk titrering av fältspatpartiklar av olika storlekar.** De partikelfraktioner, som erhöles vid den ovan nämnda centrifugeringen och sedimenteringen av suspensioner, underkastades elektrometriska titreringar till  $p_H = 3$ . Därvid bestämdes alltså de mängder vätejoner, som förmådde reagera med bestämda mängder fältspatpartiklar av viss, känd, genomsnittlig storlek. Det visade sig att partiklar av diameter över 2  $\mu$  angripas blott obetydligt. Partiklar av genomsnittlig diameter 0.4—0.5  $\mu$  sönderdelas av vätejonerna i en omfattning motsvarande 11—17 %. Partiklar av dimensioner mellan dessa ytterligheter visa en häremot svarande sönderdelning. Vid fortsatt behandling med vätejoner vid  $p_H = 3$  förededde emellertid grövre partiklar en större efterverkan än finare. Mikroclin och oligoklas förhöllo sig på ungefär samma sätt.

**De erhållna resultatens betydelse ur skogsmarksforskningens synpunkt.** De utförda undersökningarna ha visat, huru de viktiga och vanliga skogsmarksmaterialen mikroclin och oligoklas förhålla sig i medier av olika surhetsgrad. De ha även visat vid vilken ungefärlig storlek mineralpartiklarna avgiva sina basiska beståndsdelar, kali och natron, resp. kalk. Den storleksgräns, över vilken snabb sönderdelning ej längre försiggår, är ungefär 0.002 mm eller med andra ord gränsen mellan lerpartiklar och grövre jordpartiklar. Ävenså var det av betydelse att konstatera, att vid fältspaters vittning i medier av samma surhetsgrad, som förekommer i skogsmarken, aluminiumjoner frigöras. De kemiska reaktioner, som sålunda kunnat belysas, höra till dem som betinga vegetationens förseende med näringssalter och som utöva inverkan på markens surhetsgrad och därmed sammanhängande förhållanden.